SOME ULTRA-VIOLET ABSORPTION SPECTRA STUDIES

BY

CHARLES RICE HARMISON, JR.

B.A., Montana State University, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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Introduction

In recent years much attention and work has been devoted to absorption spectra studies. Such studies have been used in clarifying molecular structure, and from these studies many theories have been developed to explain color of materials.[1,2,3,4,5]

At the present time the theories pertaining to colors of inorganic compounds attribute the various absorption bands to vibrational excitation,[7,10] to electronic excitation,[9,10] to combinations of these two,[9,10] to coordination bonds [8,10] and to electronic excitation in unsaturated electron shells.[6, 10] Recently Fajans has correlated the color of a salt with the deformability of the cation and anion making up the salt.[11] Lifschitz[12] and Pauling[5] have noticed a relation between color and bond type (covalent and ionic). Inorganic coordination compounds are almost always colored, and have absorption spectra characteristic of their configuration, and the groups in the molecule. Thus a study of the absorption spectra of inorganic compounds gives a key to the structure of their molecules.

Modern theories explain organic color from two concepts. One is that absorption frequencies of a molecule are changed to frequencies of visible light when a chromophore is substituted into the molecule; the color is intensified by further substitution of an auxochrome.[13,14] The introduced chromophores often have characteristic absorption bands that are shifted a little by the group bonded to the chromophore. The second cause of color in organic molecules is the resonance between various structures; resonating molecules show strong absorption peaks, often in the ultra-violet. When a para-substituted molecule has among its resonance forms ionic configurations, there is a marked increase in absorption.[4] 2,2′ substituents of biphenly if large enough will prevent coplanarity of the two rings, and decrease inter-ring resonance. This decrease in resonance causes a corresponding decrease in intensity of absorption; determination of absorption of biphenyl derivatives gives a measure of the degree of co-planarity or resonance in the molecules.[3, 15, 16] Hence organic

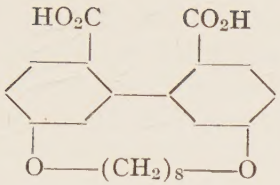
molecules also have absorption spectra that are characteristic of their structure and composition.

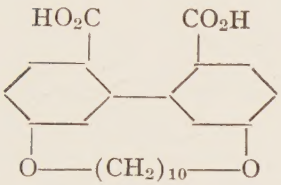
Experimental

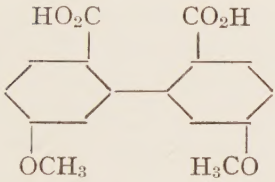
The instrument used was the Bausch and Lomb medium quartz spectrograph equipped with the same company's sector photometer. The light source was a 25,000 volt condensed spark between tungsten steel electrodes. Eastman I-O ultra-violet sensitized plates and D-C ortho plates were used. Standard developing and fixing solutions, and two common types of absorption cells with optically plane quartz end plates were used. Table I has a list of the compounds studied, and the important characteristics of the absorption curves.

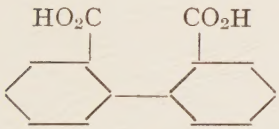
TABLE I

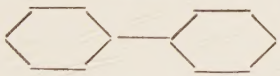
Compound	Minima	Maxima
1. $CuSO_4$-NH_3	4000 Å in .05, .1, .25 M $CuSO_4$.	None; solution becomes opaque below 2800 Å.
2. Hydrazine sulfate ($N_2H_6SO_4$)	No maxima or minima; solution becomes opaque as wave length decreases (2800-2300-Å).	
3. $CuSO_4.(N_2H_5)_2\ SO_4$	Same as hydrazine sulfate.	
4. $Co(N_2H_4)_3\ SO_4$	3200, 4400 Å.	3600-3700 Å.
5. $[Co(NH_3)_5SO_4]Cl$	3200-3400, 4200 Å.	3600 Å.
6. $[Co(NH_3)_5Cl]SO_4$	3150, 3650, 4180 Å.	3200-3600, 3760 Å.
7. $[Co(NH_3)_6]$-$[Co(NO_2)_6]$	2670, 3320, 4000 Å.	3020, 3450 Å.
8. $K_2[Co(CNS)_4]$	3700 Å.	Shoulders at 2720, 3020Å
9. $[Ni(NH_3)_6]I_2$	Indicated at 3100 Å.	3550 Å.
10. $[Ni(NH_3)_6]I_n$	2630, 3200, 4000 Å.	2900, 3500, 4660 Å.
11. KI_3	2630, 3200, 4000 Å.	2900, 3500, 4660 Å.

12.  None. 2600 Å.

13.  None. 2600 Å.

14.  None. 2600 Å.

15.  2690 Å. 2800 Å.

16. $HCOOC_3$  $COOCH_3$ 2870 Å. None.

17. Chromium leucine complex	3300, 4660 Å.	4140 Å.
18. Chromium isoleucine complex	One indicated at 3300 Å.; 4740 Å.	4140 Å.
19. Chromium glycine complex	3300, 4600 Å.	4140 Å.
20. Chromium phenyl alanine complex	3200 (?), 3600 Å.	4140 Å.
21. Glycine	Completely transparent.	
22. Leucine	Completely transparent.	
23. Phenyl alanine	None.	about 3200 Å.

For compounds 1 through 8 conductivity water was the solvent. For 9, 6-7 molar ammonia was used. For 10 and 11 spectroscopically purified alcohol[19] was used for some of the studies, and conductivity water for others. For 12 through 16, the purified alcohol was again used. For the amino acid complexes and the amino acids (17 through 23) 98% sulfuric acid was the solvent.

Discussion of Results

The studies on copper sulfate-ammonia mixtures show that for a fixed concentration of copper sulfate, the solution becomes more transparent in the ultra-violet as the ammonia concentration increases. The explanation given is that the $Cu(H_2O)_4^{++}$ ions are replaced by more transparent $Cu(NH_3)_4^{++}$ ions, ions of intermediate composition, and ions with five or six ammonia molecules per copper ion. These studies also show that the absorption curves for .01 molar copper sulfate with 6.7 molar ammonia and .01 molar copper sulfate with .2 molar ammonia ammonia should not cross as Ley and Vanheiden[17] show, but are clearly separated.

Studies on the compound written as $Cu(N_2H_5)_2\ (SO_4)_2$ show it is a double salt whose formula should be written $CuSO_4 \cdot (N_2H_5)_2SO_4$. Studies on the cobalt compound written as $CoSO_4 \cdot 3N_2H_4$ show it is a coordination compound whose correct formula is $Co(N_2H_4)_3.SO_4$.

Absorption spectra of $[Co(NH_3)_5SO_4]Cl$, $[Co(NH_3)_5Cl]SO_4$, $[Co(NH_3)_6]$ $[Co(NO_2)_6]$, and K_2 $[Co(CNS)_4]$ are given. The first two have the same general type of absorption curves, but differ slightly in position of maxima and minima. $[Co(NH_3)_6]$ $[Co(NO_2)_6]$ shows an absorption considerably modified from that of its component ions. Dilute solutions of $K_2[Co(CNS)_4]$ show the absorption of $Co(H_2O)_6^{++}$ as is to be expected from the pink color of the solution and results from electrolysis.[18]

Nickel hexammino polyiodides resemble KI_3 in their absorption spectra, and the conclusion is that all iodine atoms in the polyiodides are held in the same manner as they are held in the tri-iodide ion.

The studies on diphenic acid derivatives indicate that there is some steric hindrance due to the two carboxyl groups on the 2,2′ carbon atoms; the increased absorption of the diphenic acid with 5,5' ether groups is

explained (on the basis of the studies to date) as due to increase in resonance because of the ether and carboxyl groups being para to one another, and thus giving rise to resonance between ionic forms.

Absorption curves of chromium-amino acid complexes show characteristic maxima and minima. Further work is needed to clarify these absorption spectra.

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VITA

The writer was born February 28, 1916 in Lewistown, Montana. He attended elementary schools in Lewistown and Winnett, Montana, and received his secondary education in the high schools at Lewistown and Great Fall, Montana, graduating from the Great Falls High School in 1933. He received his undergraduate college training at Montana State College (1933-1935), Intermountain Union College (1935-1936), and Montana State University (1936-1937). He held scholarships in his sophomore and junior years and received the B.A. degree "with honors" from Montana State University in 1937. He enrolled in the Graduate School of the University of Illinois in September, 1937. He held part-time assistantships in inorganic chemistry for that year and the two succeeding years. He is a member of Phi Eta Sigma and Pi Mu Epsilon.